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(72) Inventors WILHELM VOGT, HERMANN GLASER and KURT SENNEWALD

(54) PROCESS FOR THE MANUFACTURE OF DIACYLOXYPROPENES

(71) We, KNAPSACK AKTIENGESELLSCHAFT, a body corporate organised under the Laws of Germany, of 5033, Knapsack bei Köln, Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement: —

The present invention relates to the production of diacyloxypropenes.

It has already been reported that unsaturated esters of carboxylic acids (acyloxyalkenes) can be produced from olefins, a carboxylic acid and molecular oxygen in contact with a carrier-supported catalyst containing metallic palladium. Commercially important vinyl acetate can be produced, for example, by reacting ethylene, acetic acid and molecular oxygen, in the gas phase. If propylene is the feed olefin, then allyl acetate is obtained in good yields. The catalyst used in carrying out the above gas phase reaction may contain further noble metals belonging to group 8 of the Periodic System, for example, ruthenium, rhodium, osmium, iridium or platinum, which may be used to supplement or replace palladium. Various proposals have already been made to the effect that palladium be used in combination with special addends to improve its activity and obtain a commercially attractive process. The activators suggested to be used include, for example, alkali metal or alkaline earth metal carboxylates or alkali metal or alkaline earth metal compounds yielding carboxylates under the reaction conditions (for example, alkali metal hydroxides or carbonates). In addition thereto, it has been suggested that the metals gold, copper, zinc, cadmium, tin, lead, manganese, chromium, molybdenum, tungsten, uranium, iron, cobalt, nickel, niobium, vanadium or tantalum be used as activators. The useful catalyst carriers include silicic acid, kieselguhr, silica gel, diatomaceous earth, aluminum oxide, aluminum silicate, aluminum phosphate, pumice, silicon carbide, spinels, asbestos or active carbon. These earlier processes are generally carried out by flowing a feed gas mixture comprising olefins, a carboxylic acid and oxygen over the catalyst, at elevated temperature and pressure. The catalyst may be used in the form of lumpy or granular material or in similar form offering no great resistance to the gas flowing therethrough, and may be placed in a tube capable of being cooled for the dissipation of reaction heat. It is also possible to use fine particulate catalyst in a fluidized bed reactor.

The reactor gases leaving the reactor can be cooled and freed under pressure from condensable fractions comprising the unsaturated carboxylic acid esters desired to be produced, unreacted carboxylic acid and water. For the condensation of the reaction products, it is more economic to operate at elevated pressure than to use costly cooling media and operate at particularly low temperatures. The crude condensate is worked up by conventional distillation, residual reaction gas being recycled to the reactor after replacement of the olefins, carboxylic acid and oxygen consumed, and optionally after prior separation of carbon dioxide which may have been formed.

Allyl propionate as an olefinic feed material has now unexpectedly been found, for example, to react with propionic acid and oxygen in accordance with the following equation:

$$CH_2=CH-CH_2OOCC_2H_5 + C_2H_5COOH + 0.5\ O_2 \xrightarrow{\text{Pd catalyst}}$$

$$[CH_2=CH-CH(OOCC_2H_5)_2 + C_2H_5COO-CH=CH-CH_2OOCC_2H_5] + H_2O$$

and produce good yields of a mixture comprising 3,3-dipropionoxypropene-(1) and 1,3-dipropionoxypropene-(1).

The unsaturated dipropionates so produced are easy to separate distillatively from unreacted allyl propionate and propionic acid.

The corresponding diisobutyroxy compounds and also mixed esters can be obtained in analogous manner by the substitution of acetic acid or isobutyric acid for propionic acid, and the use of allyl acetate or allyl isobutyrate, provided that acetic acid is not reacted with allyl acetate.

As reported in U.S. Patent 2,840,503, the unsaturated dicarboxylates described hereinabove can successfully be used for the extermination of phytopathogenic organisms, such as fungi, nematodes and bacteriae.

The reaction disclosed in the present invention takes an unexpected course as demonstrated firstly by the non-occurrence of an acetylizing oxidation, when vinyl acetate, acetic acid and oxygen are the feed material, and secondly by a distinctly more reluctant vinyl acetate-formation from ethylene, acetic acid and oxygen, when vinyl acetate is added to the feed mixture.

The present invention relates more particularly to a process for the manufacture of diacyloxypropenes, which comprises reacting an allyl ester of the formula:

$$CH_2=CH—CH_2OOC—R—H,$$

in which R stands for one of the groups

$$—CH_2—;$$

$$—CH_2—CH_2—;$$

or

$$CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}—CH_3,$$

with acetic acid, propionic acid or isobutyric acid and molecular oxygen, provided that when R stands for the group

$$—CH_2—$$

the acid used is propionic acid or isobutyric acid, the reaction being carried out in gas phase, optionally in the presence of one or more inert gases, at temperatures of between 100 and 250°C, preferably between 150 and 220°C, under pressures of between 1 and 20 atmospheres absolute, preferably between 5 and 10 atmospheres absolute, and in contact with a carrier catalyst containing metallic palladium, a carrier and, optionally, one or more activators.

The useful carriers and activators include those specified hereinabove.

Example

Dipropionoxypropenes

1 kg (=1.85 liters) of a spheroidal silicic acid carrier (particles of 5 to 6 mm in diameter) was mixed with a solution containing 11 grams noble metal ions, namely 8 grams Pd^{++} in the form of $PdCl_2$ and 3 grams Au^{+++} in the form of $H(AuCl_4)$, and thoroughly impregnated therewith. The quantity of liquid was selected just to permit substantially complete absorption thereof by the carrier. The mass was then dried with agitation in order to ensure uniform distribution of the noble metal salts on the carrier. The dry mass was successively introduced into a hydrazine hydrate solution rendered alkaline by means of a potassium hydroxide solution. Following complete reduction of the noble metal compounds to the corresponding noble metals, supernatant liquid was poured off, the mass was thoroughly after-washed using distilled water, and the mass was impregnated while moist with a 15% aqueous potassium acetate solution, the solution was decanted and the mass was dried at 60°C under vacuum. The catalyst so prepared was ready for use. It contained about 0.7 by weight percent Pd, 0.26 weight percent Au and 4 weight percent K in the form of potassium acetate.

1.8 cubic meters per hour of a gas mixture composed of 8% by volume oxygen, 17.8% by volume propionic acid, 3.2% by volume allyl propionate, 56% by volume nitrogen and 15% by volume carbon dioxide was passed through a catalyst furnace, which formed part of a commercial cycle system and contained 4 litres of the catalyst having the composition described hereinabove. The reaction pressure was 6.3 atmospheres absolute and the reaction temperature was 185°C. This corresponded to a velocity of flow of 73.4 cm/second and a contact time of 7.56 seconds, in the reactor. The resulting reaction gases were condensed and the condensate was successively distilled. 280 grams/hr high-boiling products were obtained. The products were composed of 3,3-dipropionoxypropene-(1) (allylidene dipropionate) and 1,3-dipropionoxypropene-(1) in the ratio of 1:5, as determined by gas-chromatography.

70 grams unsaturated dipropionates were found to have been formed per liter of catalyst, per hour.

WHAT WE CLAIM IS:—

1. A process for the manufacture of diacyloxypropenes, which comprises reacting an allyl ester of the formula:

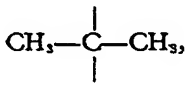
$$CH_2=CH—CH_2OOC—R—H,$$

in which R stands for one of the groups

$$—CH_2—;$$

$$-CH_2-CH_2-;$$

or



with acetic acid, propionic acid or isobutyric acid and molecular oxygen, provided that when R stands for the group

$$-CH_2-$$

the acid used is propionic acid or isobutyric acid, the reaction being carried out in gas phase, optionally in the presence of one or more inert gases, at a temperature of between 100 and 250°C, under pressures of between 1 and 20 atmospheres absolute, and in contact with a carrier catalyst containing metallic palladium, a carrier and optionally one or more activators.

2. A process as claimed in claim 1, wherein the said temperatures are between 150 and 220°C.

3. A process as claimed in claim 1 or 2, wherein the said pressures are between 5 and 10 atmospheres absolute.

4. A process for the manufacture of dipropionoxypropenes conducted substantially as described in the foregoing Example.

5. Diacyloxypropenes whenever obtained by a process as claimed in claim 1, 2, 3 or 4.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24, Southampton Buildings,
Chancery Lane,
London, W.C.2.

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